

# *The Temperature Dependence of Spectral Broadening in the Hg ( $6^1S_0-6^3P_1$ ) Multiplet At High Optical Densities*

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A new method has been developed for determining rapidly changing translational temperatures in a gas that has been heated by such transient phenomena as the passage of a shock wave or the absorption of sub-microsecond pulses of radiation from an infrared laser. The method depends upon the use of trace amounts of Hg vapor and its absorption of radiation in the neighborhood of the 253.7 nm isotopic and hyperfine multiplet. As the Hg atoms sense changes in the translational temperature of the host gas, the absorption of 253.7 nm radiation also changes by virtue of the Doppler and Lorentz broadening of the multiplet lines. Emission spectra of a Hg discharge light source in the neighborhood of 253.7 nm were shown to be

readily simulated by a two zone computer model even at large optical densities. The same lamp parameters that were used in these calculations could also be used to simulate the experimental pressure and temperature dependence of the total integrated absorption. This provided a means for obtaining the temperature calibration curves needed to monitor the changing translational temperature of a gas undergoing rapid heating or cooling.

**Key words:** absorption; atoms; calibration; Hg; lamp; line profile; radiation; resonance; temperature dependence; transient heating.

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## **1. Introduction**

A new method for determining transient translational gas temperatures has been developed. It involves the use of small concentrations of Hg atoms to monitor the translational energy associated with molecules of the host gas. For example, after undergoing rapid vibrational excitation, the host molecules collisionally equipartition the deposited energy and the monatomic Hg tracer senses the increase in translational temperature. Such vibra-

tional excitations are usually achieved by the absorption of a laser pulse either in the ultraviolet (electronic excitation followed by rapid internal conversion to the ground electronic state) or directly by absorption of an intense laser pulse in the infrared. The passage of a shock wave through the gas on the other hand, rapidly increases the translational temperature so that the process of equipartition results in an increase in rotational and vibrational energies and is accompanied by the net decrease in the translational temperature which the Hg atoms monitor. The relaxation time constants for these processes provide a means for directly determining the efficiency with which energy is transferred between molecules by collisional processes.

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A Hg atom can be used to detect changes in the translational temperature of a surrounding gas by noting the quantitative features of the absorption spectrum in the neighborhood of the resonance transition at 253.7 nm ( $6^1S_0-6^3P_1$ ). This spectrum is complex because of the natural isotopes of Hg and the hyperfine structure of the odd numbered ones. The absorption of radiation in this region changes with translational temperature due to Doppler and Lorentz (collisional) line broadening. It will be shown that both the pressure and temperature dependence of the absorption can be calculated by matching the high resolution spectrum of the light source with a computer model that takes into account both the Doppler and Lorentz effects [1].<sup>1</sup>

It has been shown previously that a simple two zone model can simulate the light emission from an atomic resonance lamp [2]. This representation is superior to earlier methods [1] in that actual lamp temperatures are used rather than unrealistically high ones that are chosen primarily to represent different emitting and absorbing atom densities in the lamp. In the two zone model, zone 1 is assumed to contain both emitting and absorbing atoms uniformly distributed. The emission from this zone, at the frequency  $\nu_r$ , is proportional to the emittance:  $J_1(\nu_r)$ , which is given by the expression

$$J_1(\nu_r) = 1 - \exp(-k_1(\nu_r)) \quad (1)$$

The Napierian absorption coefficient  $k_1(\nu_r)$ , for a Lorentz broadened Doppler line is defined in the appendix. The second zone, which is assumed to contain only ground state Hg atoms, absorbs some of the radiation from zone one and transmits radiation proportional to the emittance. Therefore  $J_2(\nu_r)$  is given by

$$J_2(\nu_r) = J_1(\nu_r) \exp(-k_2(\nu_r)) \quad (2)$$

This quantity is proportional to the radiation emitted by the lamp so that when it is attenuated by an absorption cell containing Hg vapor, the transmitted radiation intensity is proportional to its emittance  $J_2(\nu_r)$ , namely

$$J_3(\nu_r) = J_2(\nu_r) \exp(-k_3(\nu_r)) \quad (3)$$

where the subscript 3 distinguishes this externally absorbing region from the lamp zones 1 and 2.

Such a two zone model description of the lamp provides a simple means of representing the actual

gradients in absorber and emitter concentrations that are always present in any lamp configuration. The results obtained with models containing more complex distributions of the absorbing and emitting atoms have been shown to be virtually indistinguishable from the idealized two zone model [3].

In earlier work [4] lamps were constructed, and emission profiles obtained, in order to determine the concentration dependence of either fluorescence or absorption signals in zone 3. In these instances optically thin lamps were used to maximize the detection sensitivity for the fluorescing and absorbing atoms. Since optically thin lamps contain low pressures of inert buffer gas, line profile simulations were made invoking Doppler broadening only. These simulations were compared with experiment either by matching the computed and observed absorption vs. concentration calibration curves (curve of growth method) [5], or by matching computed emission profiles with high resolution emission spectra of the lamp (direct method) [6,7].

In the present work we have used the resonance absorption phenomenon to determine transient translational temperatures over a wide dynamic range. The two zone model was extended to very large optical depths ( $>1000$ ), using all of the multiplet components of the Hg resonance line with only Doppler and Lorentz broadening effects incorporated into the computations.

## 2. Experimental

Two types of resonance lamps were used. An unreversed lamp with a low value of optical depth was constructed by placing a drop of mercury in a 12 mm o.d., 15 cm long quartz tube which had been previously evacuated and baked. After addition of the mercury, the tube was evacuated again, filled with argon to a pressure of about 4 Torr and sealed. An electrodeless, microwave ( $\sim 2.5$  GHz) discharge was initiated and maintained at 5 watts. After the discharge stabilized, the lamp assembly was cooled with a stream of compressed air and the radial emission focused onto the entrance slit of a spectrograph with a resolution of  $1.6 \times 10^6$ . Under microdensitometer examination the exposed photographic plates showed five very narrow, unreversed Hg multiplet lines in the neighborhood of 253.7 nm.

A second lamp, suitable for operation at large optical depths, consisted of a commercial, single ended, pencil-like lamp that contained a drop of mercury in about 100 Torr of argon. It consisted of

<sup>1</sup> Figures in brackets indicate literature references.

a dual bore fused silica tube 5.4 cm long and 6 mm o.d. with both electrodes mounted and sealed at one end. Power for the lamp was supplied by a filtered dc power supply (450 volts) in series with a current regulating circuit. The lamp current was adjustable between 5 and 20 mA without significant destabilization at the low current extreme. A hollow brass cylinder 16 mm o.d., 10 mm i.d., and 8 cm long was used as a heat sink and enclosed the lamp assembly. A 3 mm hole was drilled perpendicular to the cylinder axis and served as a collimating aperture for the light source. Stable operation required a constant lamp temperature since a change of one degree resulted in about a 15% change in Hg pressure and hence in the lamp's optical depth. As a result good voltage and current regulation of the power supply, and high thermal stability of the lamp were found to be necessary for satisfactory absorption measurements to be made.

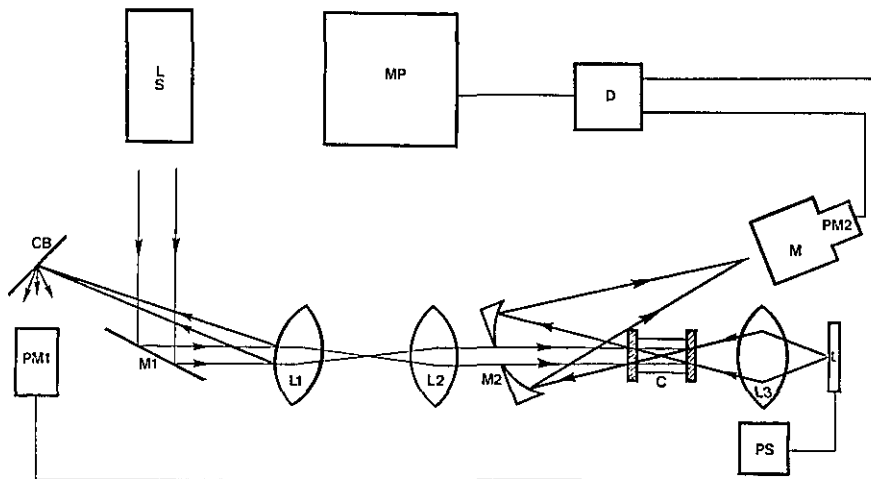
The high resolution lamp spectra were photographed with Kodak SWR spectroscopic plates that were calibrated by exposure at constant density for known times and examined with a microdensitometer so that plate density-exposure curves could be obtained. These showed the expected departure from reciprocity at short exposures, saturation at long exposures, and linear behavior over a considerable range of median exposures.

Absorption measurements were performed as follows: the high optical density Hg lamp was partially focused through the center of a Hg-containing absorption cell that was 5 cm long. The emerging beam was focused onto the entrance slit of a low resolution f/6 grating monochromator set at 253.7 nm with a 1P28 photomultiplier positioned at the exit slit. The output of the photomultiplier was connected to a preamplifier whose input

impedance was 1000 ohms and whose 50 ohm output impedance was matched to the input of a digitizer that was set in a continuous sweep mode. For a known gain of the digitizer's input amplifier, a digitized voltage offset could be adjusted to null the constant signal displayed on an oscilloscope. The value of this offset voltage ( $S_0$ ) was proportional to the intensity of the lamp. When 1.8 mTorr of Hg (vapor pressure at 298 K) was introduced into the absorption cell, the null point shifted to a lower value of the offset voltage ( $S_1$ ) which is proportional to the light intensity reduced by the Hg absorption. Thus the fraction of the 253.7 nm radiation absorbed is given by  $(S_0 - S_1)/S_0$ . The accuracy of this quantity is limited primarily by the signal noise and the 1% resolution of the offset control. Longterm stability, as determined by a set of successive absorption measurements, was found to vary within  $\pm 2\%$  of the mean. The linearity of the detection system was verified by attenuating the 253.7 nm beam with calibrated neutral density filters.

The apparatus, shown schematically in figure 1, was used to monitor transient temperature excursions. A CO<sub>2</sub> TEA laser irradiated the absorption cell which contained a trace of Hg vapor and an infrared absorbing gas such as SF<sub>6</sub>. Pressures were measured with a capacitance manometer. A fraction of the laser beam was reflected from the front surface of the first lens and focused onto a carbon block. A visible incandescent light pulse with a 50 ns rise time was thus produced and triggered the digitizer. The output signal was computer averaged for as many sweeps as was necessary to produce a satisfactory signal to noise ratio. Absorption of the resonance radiation by Hg vapor could thus follow temporal changes in the translational temperature of gases in the absorption cell.

Figure 1—Schematic diagram of the apparatus used to transiently heat SF<sub>6</sub> and to measure its translational temperature. LS is the CO<sub>2</sub> TEA laser; M1 is a reflecting mirror; L1 is a partially reflecting tilted lens; L2 is a collimating lens; M2 is a split, curved mirror with the center section removed; C is a narrow bore absorption cell containing BaF<sub>2</sub> windows (connection to vacuum line not shown); L3 is a lens for focusing radiation from the Hg resonance lamp L; PS is a regulated DC power supply; M is a low resolution f/6 monochromator; PM2 is a 1P28 photomultiplier; D is a fast digitizer; MP is a microcomputer; CB is a carbon block that incandesces when irradiated by the CO<sub>2</sub> laser and is used to trigger the digitizer by means of the photomultiplier PM1.



### 3. Results and Discussion

#### 3.1 The Hg Multiplet Spectrum and Its Computer Simulation

To assess how well the two zone model describes the emission spectrum from typical resonance lamps, a number of high resolution spectra were recorded. Figure 2 shows examples of emission in the neighborhood of 253.7 nm for three different lamp conditions. Frame C is the unreversed spectrum of an optically thin lamp. It shows the 10 isotopic and hyperfine components of the 253.7 nm Hg multiplet resolved into five lines that exhibit overlap only as a result of natural and Doppler broadening. The instrument resolution ( $1.6 \times 10^6$ ) was capable of resolving lines that are about a Doppler width apart ( $0.022 \text{ cm}^{-1}$  at 298 K). As a result five partially overlapping lines were readily resolved. The line due to the Hg(196) isotope was not observed because of its very low natural fractional abundance (0.0015). Its position is in the vacancy in what appears to be an otherwise equispaced ( $0.15 \pm 0.02 \text{ cm}^{-1}$ ) spectrum. The spectra shown in figure 2 were not corrected for plate response non-linearities. The exposures however did not depart very much from the linear regime so that the recorded peak heights are a good approxi-

mation of the relative intensities. These amplitudes are in agreement with values from the literature [8] and hence were used with some confidence in the computer program.

The high optical density lamp, operated with currents of 6 and 8 mA (frames B and A in fig. 2), shows marked self-reversal that becomes greater as the current increases and raises the lamp temperature and Hg pressure. The intensities adjacent to each of the multiplet lines changes the five line unreversed spectrum into a complex six line structure whose two outermost lines are the self-reversed wings of the two extreme lines of the unreversed quintuplet. It is clear that less of the resonance radiation emitted by the reversed lamp is absorbed by Hg vapor because of lower emission at the actual multiplet line positions. When absorption is used to determine temperature changes over a wide range, a reversed resonance lamp is the preferred choice since saturation (approach to 100% absorption) occurs with an unreversed lamp even when the optical density in the absorption cell is small.

Figure 3 shows how well a computer-simulated emission from a two zone lamp model can be made to fit an experimental spectrum. Lamp conditions and model parameters are given in the figure caption and the experimental spectrum was corrected for nonlinear plate response. Except for a difference in scale, the experimental and computed spectra are seen to be very similar with regard to line spacing and overall width. The differences in line intensities are worth noting because any further incremental changes in the model parameters did not significantly improve the agreement. The simulated spectrum shows less change in the relative peak heights and more variation at the minima than does the experimental spectrum. The reason for this undoubtedly resides in the inability of the two zone model to accurately represent the actual distribution of emitters and absorbers in the lamp.

In order to obtain an optimum match between the computer simulation and the experimental lamp emission, four parameters are required to initialize the two zone model. They are  $A_1$  and  $A_2$ , the ratio of Lorentz to Doppler widths in zones 1 and 2;  $OD_1$ , the optical depth in zone 1; and  $R$ , the ratio of optical depths in zone 1 to zone 2. The quantity  $A_3$ , the ratio of Lorentz to Doppler widths in the absorbing region 3, has been determined previously for Hg broadened by Ar [8]. It is proportional to the argon pressure and is equal to 1.0 at a pressure of about 140 torr. Since the argon pressure in the lamp was close to this pressure,  $A_1$  and  $A_2$  were assumed to be unity for all experimental lamp conditions. The quantities  $OD_1$  and  $R$  on the other

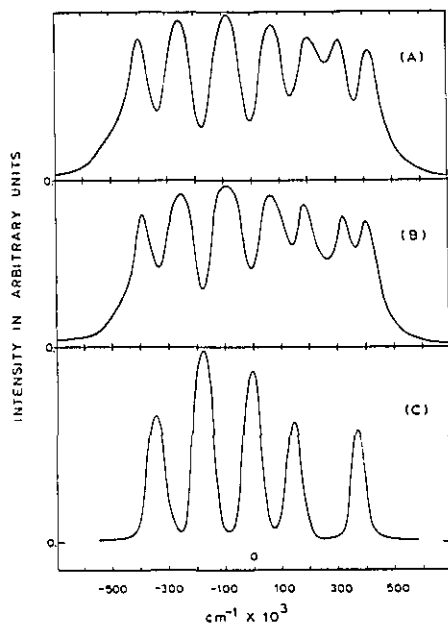
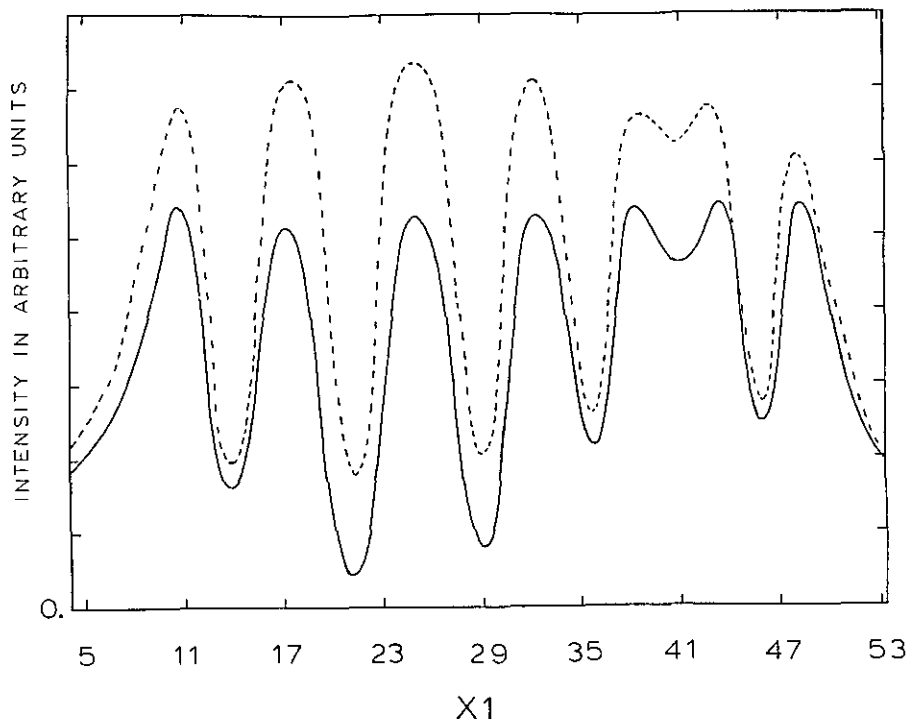


Figure 2—Frame C—A microdensitometer trace of a photographic plate showing the high resolution spectrum obtained for an optically thin, unreversed electrodeless Hg discharge lamp in the neighborhood of 253.7 nm.

Frame B—The spectrum of a reversed lamp produced by a dc discharge operated at a well regulated current of 6 mA in the same spectral region.

Frame A—The spectrum in the same spectral region of the same lamp operating at 10 mA.

Figure 3—A microdensitometer trace that has been corrected for plate nonlinearities (dashed curve), of the high resolution spectrum emitted by the reversed Hg lamp operated at 9 mA. This is to be compared with the calculated lamp profile (solid curve) using the following lamp parameters:  $A_1=A_2=1$ ;  $OD_1=60$  and  $R=3$ .



hand, increase as the lamp current or temperature does because the Hg concentration and its gradient near the lamp walls are determined by these parameters.

### 3.2 Absorption Measurements and Their Computer Simulation

A detailed comparison of the calculated and measured integrated absorption by Hg vapor as a function of temperature and buffer gas pressure is of interest. While the computer simulated lamp emission profiles do not quite match the observed ones, it will be seen that the optimized model parameters so obtained, can be used to compute the temperature and pressure dependence of the absorption of 253.7 nm radiation quite well.

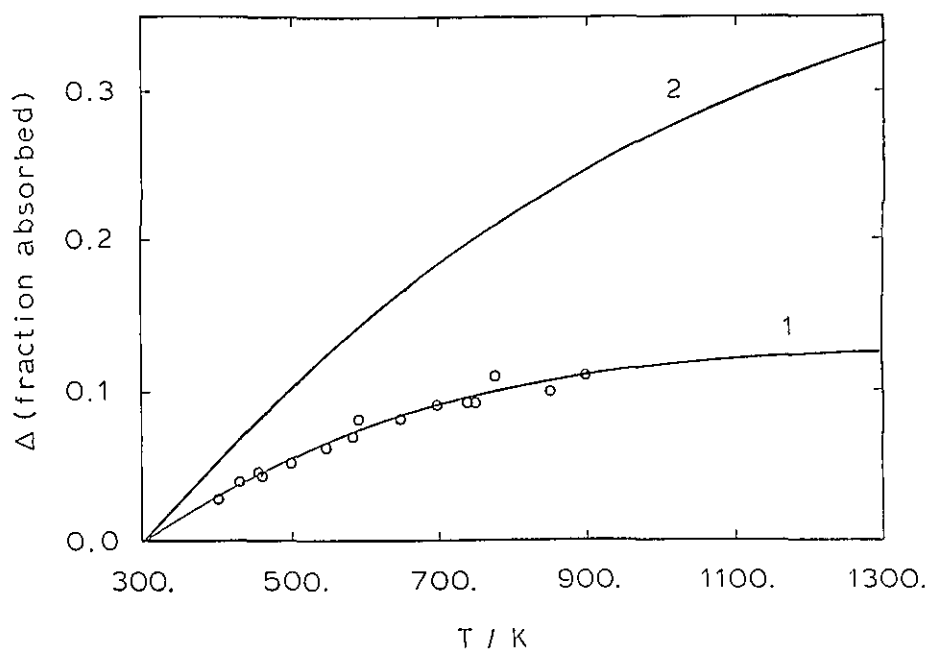
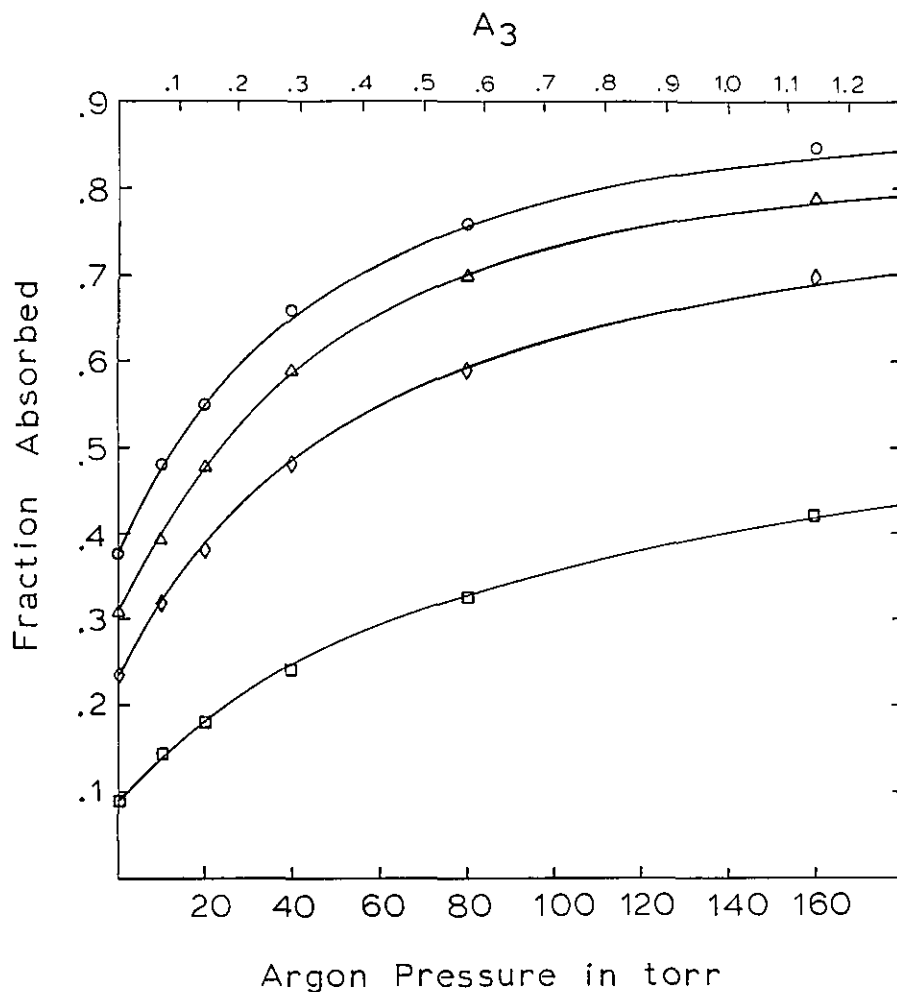
As mentioned above, the ratio of Lorentz to Doppler widths ( $A$ 's) for the  $6^1S_0-6^3P_1$  Hg transition is unity when about 140 torr of argon is present as a buffer gas. Figure 4 shows experimental points plotted on a graph of fraction absorbed vs.  $A_3$  and Argon pressure for four different lamp currents of 8, 10, 15 and 20 mA. The solid curves were calculated by means of the two zone lamp model. As discussed earlier the quantities  $A_1$  and  $A_2$  were assigned the constant value of one while  $OD_1$  and  $R$ , representing emitter and absorber concentrations and their gradients, were increased as the lamp current was made larger. The values of

$OD_1$  and  $R$  were identical to those required to produce the best agreement with the experimental profile in figure 3. It should be noted that this computer simulation of the pressure growth curves is quantitatively better than that obtained for the lamp emission spectra.

Hg absorption data were obtained over a range of temperatures (300–900 K) by means of an electrically heated copper furnace that housed a Hg containing absorption cell. The heated portion of the cell was an evacuated fused silica cylinder that was connected to a small tube outside of the furnace. This tube (<2% of the total volume) contained a small pool of liquid mercury thermostated at 298 K. The heated absorption cell therefore contained 1.8 mTorr of Hg vapor at all furnace temperatures with a number density of Hg atoms that was inversely proportional to the furnace temperature. The 253.7 nm radiation (supplied by a reversed lamp operated at 9 mA) traversed the cylindrical absorption cell perpendicular to its axis, and was measured by the 1P28 photomultiplier-monochromator system. Curve 1 in figure 5 was calculated from an appropriate set of model parameters obtained earlier and is seen to agree well with the experimental data points. Curve 2 was calculated for a gas heated at constant volume of Hg atom number density. Figure 6 shows a set of temperature calibration curves that were calculated for the same set of lamp parameters used in figure 4. These

**Figure 4**—Measurements of fractional absorption as a function of argon pressure in a Hg absorption cell containing 1.8 mTorr of Hg vapor. The reversed Hg discharge lamp was used operating under the following conditions: 8 mA—circles; 10 mA—triangles; 15 mA—diamonds; and 20-mA squares. The solid curves are lamp simulation calculations of  $J_3$  vs.  $A_3$ , where  $A_3=1$  when  $P_{(AR)}=140$  Torr. In all calculations  $A_1=A_2=1$ ,  $T_3=300$  K, and  $OD_3=185$ .

Curve 1. (circles)  $OD_1=40$ ,  
 $R=2$   
 " 2. (triangles)  $OD_1=80$ ,  
 $R=4$   
 " 3. (diamonds)  $OD_1=190$ ,  
 $R=10$   
 " 4. (squares)  $OD_1=1050$ ,  
 $R=40$



**Figure 5**—Experimental data (plotted points) and computer simulated curves of fraction absorbed vs. temperature.

Curve 1. Hg vapor at a constant pressure of 1.8 mtorr  
 " 2. Hg vapor at a constant Hg atom number density of  $5.8 \times 10^{13} \text{ cm}^{-3}$  (1.8 mtorr and 298 K)

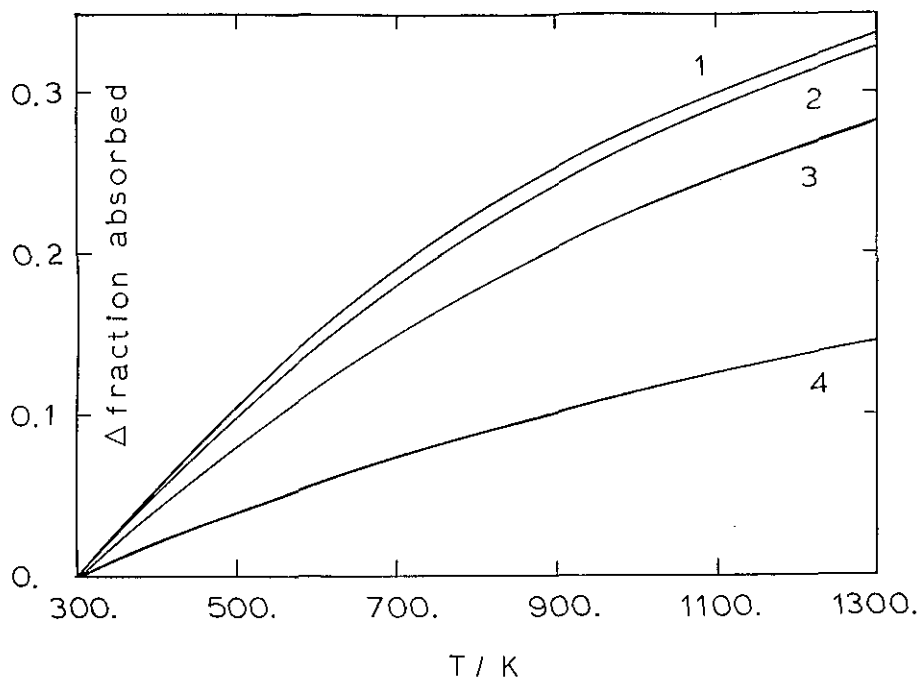


Figure 6—Computed fraction absorbed vs. temperature curves for a Hg absorption cell containing 1.8 mTorr of Hg vapor and using the same lamp parameters as those given in figure 4.

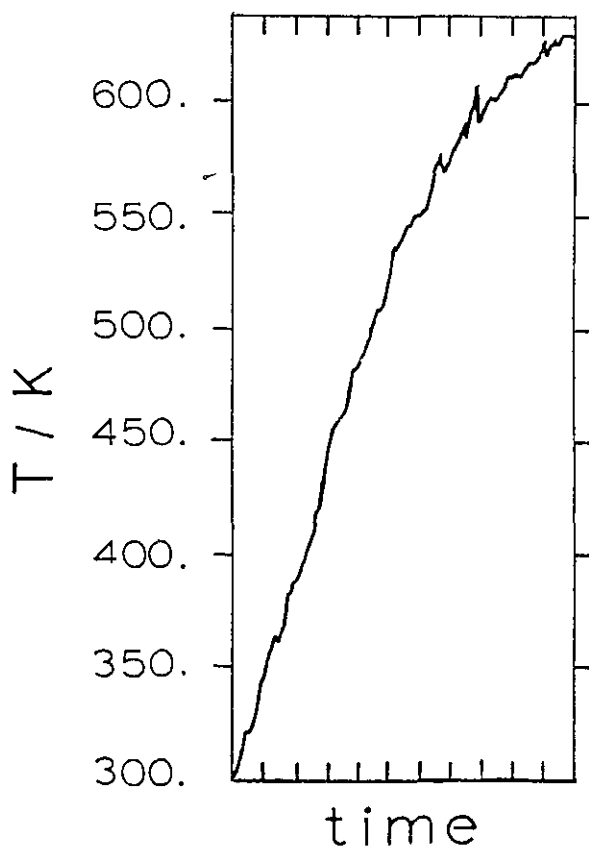


Figure 7—An experimental temperature-time curve for one Torr of a transiently heated 50:1 mixture of  $\text{SF}_6$  and Hg vapor.  
 $T_{\text{eq}} = 836 \text{ K}$ ,  $0.8 \mu\text{s}/\text{time div.}$ , 400 sweeps averaged.

curves cover a wide range of lamp optical densities and provide a basis for transient temperature measurement over large dynamic ranges.

### 3.3 Temperature Modulation Experiments

A typical case of constant volume heating is illustrated in figure 7 which shows a typical signal averaged curve for the temporal dependence of absorption of 253.7 nm radiation by 1.8 mTorr of Hg vapor mixed with 1 Torr of  $\text{SF}_6$ . At  $t=0$ , a 500 ns, 1 Joule pulse of  $10.6 \mu\text{m}$  radiation from a  $\text{CO}_2$  laser was absorbed by a 5 cm path through  $3 \text{ cm}^3$  of the  $\text{SF}_6$ -Hg mixture. About  $25 \mu\text{s}$  after the laser pulse the vibrational excitation of the irradiated  $\text{SF}_6$  becomes equipartitioned with its rotational and translational degrees of freedom. As the average translational energy of the  $\text{SF}_6$  increased and the Hg atoms responded to this change, absorption of the 253.7 nm multiplet was broadened and became larger. The temperature scale shown in figure 7 was obtained from the parameters used to compute the temperature calibration curves in figure 5 and 6.

## 4. Conclusions

It is well known that the absorption of resonance radiation by an atomic gas is both pressure and temperature dependent because of the line broadening brought about by molecular collisions and

the Doppler effect. In particular, it has been shown here that the amount of resonance radiation absorbed in the neighborhood of 253.7 nm by a trace of Hg vapor is a measure of its translational temperature. When admixed with a gas such as SF<sub>6</sub>, the Hg atoms can monitor the temperature changes that occur in the combined system after a 10.6 μm pulse from a CO<sub>2</sub> TEA laser is absorbed by the SF<sub>6</sub>.

The multiplet emission in the neighborhood of 253.7 nm by a high optical density Hg light source was simulated by a simple two zone model. The natural line widths were enhanced by Doppler and

Lorentz broadening. Two fixed and two adjustable parameters were required to describe a wide variety of lamp conditions. It was shown that the same lamp parameters that optimized the fit of the light source emission spectra could also be used to calculate the total integrated absorption as a function of both pressure and temperature. The agreement obtained between the simulation and the experimental pressure and temperature data shows that computer derived temperature calibration curves for different lamp conditions are a reasonable basis for making transient temperature measurements in rapidly heated gases.

## APPENDIX

The following describes the line shape and absorption calculations discussed above. The reader is referred to Mitchell and Zemansky for further details [1].

We designate  $k(\nu_r)$  as the Napierian absorption coefficient for an isolated Doppler line which is broadened by pressure (Lorentz broadening). This quantity is the contribution of the entire Doppler line at wavelength  $\nu = \nu_r$  as convoluted by a Lorentzian function and is given by the following expression:

$$I. \quad k(\nu_r) = k(\nu_0) \int_{-\infty}^{+\infty} \frac{e^{-\left[\frac{\nu - \nu_0}{\delta}\right]^2}}{1 + \left[\frac{\nu - \nu_r}{\Delta}\right]^2} d\nu$$

where  $\nu_r$  is some chosen reference frequency and  $\nu_0$  is the frequency at the center of the doppler line. The quantity  $\delta$  is the Doppler half width (half line width at maximum/e) and  $\Delta$  is the Lorentz half width (half line width at maximum/2) and  $k(\nu_0)$  is the Napierian absorption coefficient at the line center.

In the following calculations we work with dimensionless units by making the following substitutions:

Set  $X = (\nu - \nu_0)/\delta$ ;  $X_r = (\nu_r - \nu_0)/\delta$ ;  $Y = (\nu - \nu_r)/\delta$ ;

$Y_r = (\nu_r - \nu_0)/\delta$ ;  $A = \Delta/\delta$

Thus:  $X = AY$  and  $X_r = AY_r$

The integral over the Doppler line function is

$$\int_{-\infty}^{+\infty} \exp(-X^2) \delta dX = \delta \sqrt{\pi}$$

and the integral over the Lorentz line function is given by

$$\int_{-\infty}^{+\infty} dX / (1 + ((X - X_r)/A)^2) = A\pi$$

With these integrals and definitions in mind we can express  $k(\nu_r)$  in dimensionless form as follows:

$$II. \quad k(X_r) = \frac{k'(0)}{\delta \sqrt{\pi} A \pi} \int_{-\infty}^{+\infty} \frac{e^{-X^2} dX}{1 + ((X - X_r)/A)^2}$$

where it is understood that an isolated resonance line is centered about  $X=0$  and the optical depth,  $OD$ , for a pure Doppler broadened line is:

$$III. \quad OD = \frac{k'(0)}{\delta \sqrt{\pi}} = n \cdot \sigma(0) \cdot \Lambda$$

The value of  $\sigma(0)$  is the absorption cross section of the pure Doppler line at its center in units of cm<sup>2</sup>,  $n$  is the molecular number density in cm<sup>-3</sup> and  $\Lambda$  is the absorption length in cm. The quantity  $\sigma(0)$  is obtained from the relation:

$$IV. \quad \sigma(0) = \frac{\pi e^2 f}{\sqrt{\pi} \cdot mc \delta} = \frac{0.50 \cdot 10^{-12} \cdot f}{\delta}$$

where  $f$  is the oscillator strength and  $\delta$ , the Doppler width, is in units of  $\text{cm}^{-1}$  and is given by:

$$\delta = \omega_0 \cdot 4.3 \cdot 10^{-7} \sqrt{T/M},$$

with  $\omega_0$  in  $\text{cm}^{-1}$ ,  $T$  in  $K$  and  $M$  is the molecular weight in g/mole.

Equation II above refers to a single emission line. For  $j$  lines the following equation applies:

$$V. \quad k(X_r) = \frac{1}{A\pi} \int_{-\infty}^{+\infty} \sum_{i=1}^j \frac{OD(i) e^{-(X-L(i))^2}}{1 + ((X-X_r)/A)^2} dX$$

where  $L(i)$  is the relative line position of the  $i^{\text{th}}$  line expressed in terms of the reduced frequency,  $X$  given above.

For each zone  $m$  in the simple model discussed in the text, the absorption coefficient  $k_m(\nu_r)$  can be calculated from equation V. In each zone, the quantities  $X$ ,  $X_2$  and  $L(i)$ 's must be expressed on an appropriate scale of reduced frequencies. Thus  $X$  takes on values  $X_1$ ,  $X_r$  and  $X_3$  which are related by  $X_1\delta_1 = X_2\delta_2 = X_3\delta_3$ . The same applies to the  $X_r$ 's and the  $L(i)$ 's. Also each zone has its own value of  $A$ , namely  $A_1$ ,  $A_2$  or  $A_3$ .

The  $OD(\text{total})$  for each zone is calculated from its temperature  $T_m$ , length and the  $f$  value for the entire transition. The  $OD(i)$ 's for each zone must satisfy,  $OD(\text{total}) = \sum OD(i)$  and the  $f$  value for the entire transition is calculated from its lifetime:  $\tau \sim 1.1 \times 10^{-7} \text{s}$ ,  $f = 0.027$ .

There are seven stable isotopes; five even and two with odd mass numbers. The latter are Hg(199) and Hg(201) with nuclear spins of 1/2 and 3/2 respectively that couple with the electron  $J$  value. The 253.7 nm multiplet is composed therefore of 10 lines: one from each of the five even mass isotopes, two from Hg(199) and three from Hg(201). The natural abundance of the Hg(196) isotope is so small that its emission is of no consequence. The five resolved lines thus consisted of the following components: [9] (frame C in fig. 2)

$\Delta\lambda/10^3 \text{cm}^{-1}$	Hg isotopes	Relative Intensities
-340	204, 199a, 201a	0.64
-180	202	1.00
0	200	0.78
150	198, 201b	0.49
385	199b, 201c	0.46

Thus the  $f$  values used in the lamp simulation calculations for each of the resolved lines are:

$$f_i = (0.027) \left[ \frac{I_i}{\sum I_i} \right] \quad \text{where } i = 1, 2, \dots, 5$$

and  $I_i$  is the relative intensity of the  $i^{\text{th}}$  resolved multiplet line.

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